

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
22 February 2001 (22.02.2001)

PCT

(10) International Publication Number  
**WO 01/12319 A1**

(51) International Patent Classification<sup>7</sup>: **B01J 21/16**,  
37/00, C04B 33/00

JONES, William: 6 Lantree Crescent, Cambridge CB2  
2NJ (GB).

(21) International Application Number: PCT/EP00/07785

(74) Agent: SCHALKWIJK, Pieter, Cornelis; Akzo Nobel  
N.V., Intellectual Property Dept. (Dept. AIP), P.O. Box  
9300, NL-6800 SB Arnhem (NL).

(22) International Filing Date: 11 August 2000 (11.08.2000)

(25) Filing Language: English

(81) Designated States (national): BR, CA, CN, IN, JP, KR.

(26) Publication Language: English

(84) Designated States (regional): European patent (AT, BE,  
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,  
NL, PT, SE).

(30) Priority Data:  
09/372,293 11 August 1999 (11.08.1999) US

Published:

— With international search report.

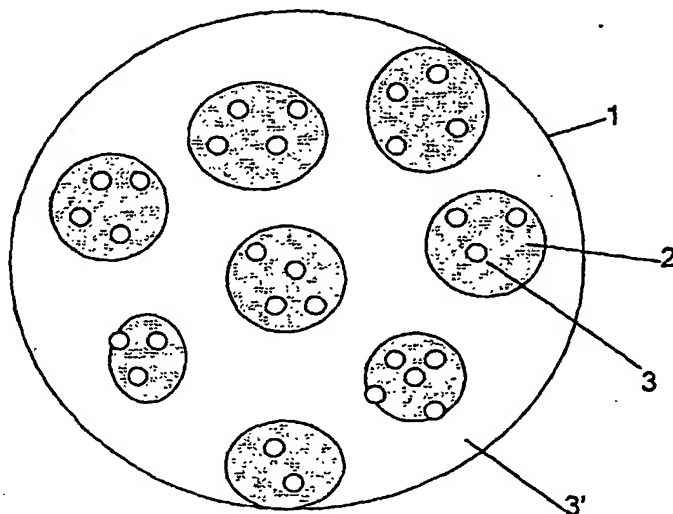
— Before the expiration of the time limit for amending the  
claims and to be republished in the event of receipt of  
amendments.

(71) Applicant: AKZO NOBEL N.V. [NL/NL]; Velperweg 76,  
NL-6824 BM Arnhem (NL).

(72) Inventors: STAMIREN, Dennis; 6 Rockingham Drive,  
Newport Beach, CA 92660 (US). O'CONNER, Paul;  
Hogebrinkerweg 9, NL-3871 KM Hoevelaken (NL).

For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(54) Title: ATTRITION RESISTANT, SHAPED, CRYSTALLINE Mg-Al-Si-CONTAINING CLAY-CONTAINING BODIES



(57) Abstract: The present invention is directed to a process for the preparation of crystalline Mg-Al-Si-containing clay-containing bodies from sources comprising an aluminium source, a magnesium source, and a silicon source, comprising the steps of: a) preparing a precursor mixture; b) shaping the precursor mixture to obtain shaped bodies; c) optionally thermally treating the shaped bodies; and d) aging to obtain crystalline Mg-Al-Si-containing clay-containing bodies. The quintessence of the present invention is that the bodies are shaped prior to the forming of the crystalline clay in said bodies. This results in very attrition resistant bodies, without the need to add a binder material. The crystalline clay is formed from an aluminium source, a magnesium source, and, a silicon source. If only an aluminium source and a magnesium source are present, hydrotalcite is formed. If an aluminium source, a magnesium source, and a silicon source are present, saponite or montmorillonite is formed.

WO 01/12319 A1

## ATTRITION RESISTANT, SHAPED, CRYSTALLINE Mg-Al-Si-CONTAINING CLAY-CONTAINING BODIES

5

The present invention pertains to shaped crystalline Mg-Al-Si-containing clay-containing bodies and a process for the preparation thereof. Examples of these types of crystalline clays include smectites such as saponite and montmorillonite. Crystalline Mg-Al-Si-containing clay has several applications in the catalyst field and as absorbents. For most commercial applications crystalline clays are formed into shaped bodies such as spheres. In all these applications where shaped bodies are exposed to severe processing conditions and environments, such as oil refinery applications, separations, purifications, and absorption processes, it is of paramount importance that the integrity of the crystalline Mg-Al-Si-containing clay-containing shaped bodies is kept intact and attrition is prevented.

In the prior art, crystalline Mg-Al-Si-containing clay is usually incorporated into binder or matrix material in order to obtain attrition resistant shaped bodies. Commonly used binder or matrix material is alumina prepared from alumina precursors such as aluminium chlorohydrate, soluble alumina salts, and acid dispersed pseudoboehmite, silica such as silica sols, silicates, silica-alumina gels, and combinations thereof.

25

However, when crystalline Mg-Al-Si-containing clay is embedded in a matrix, the amount of active crystalline clay ending up in the resulting shaped bodies is relatively small. There are applications in which for performance reasons it is desired that the shaped bodies consist or mostly consist of active crystalline clay. Also, by the incorporation of crystalline Mg-Al-Si-containing clay into matrix material, physical properties of the crystalline clay such as specific surface area, pore size distribution, etcetera may be detrimentally affected.

30

Further, the distribution of the crystalline clay within the matrix is difficult to control. Another disadvantage of having to use a matrix to obtain attrition resistant bodies is the fact that most commonly used matrix/binder materials have some chemical activity, which in certain applications can cause undesirable side reactions. For instance, the one of the most commonly used binder material in FCC catalysts and additives is silica or silica based material. These types of binders are not suitable for use in sulphur oxides removal additives, because they detrimentally affect the sulphur removal.

The present invention provides crystalline Mg-Al-Si-containing clay-containing bodies which are attrition resistant without high amounts of binder having to be present. In fact, crystalline Mg-Al-Si-containing clay-containing bodies are provided which can be binder-free. The crystalline clay distribution within the crystalline Mg-Al-Si-containing clay-containing bodies of the invention can easily be controlled as will be explained further in the description. Within the context of the present specification, the term "crystalline clay" means a clay which gives an X-ray diffraction pattern characteristic of the specific type of synthetic clay.

The present invention is directed to a process for the preparation of crystalline Mg-Al-Si-containing clay-containing bodies from sources comprising an aluminium source, a magnesium source, and a silicon source, comprising the steps of:

- a) preparing a precursor mixture,
- b) shaping the precursor mixture to obtain shaped bodies,
- c) optionally thermally treating the shaped bodies, and
- d) aging to obtain crystalline Mg-Al-Si-containing clay-containing bodies.

The quintessence of the present invention is that crystalline Mg-Al-Si-containing clay is formed after shaping. This results in very attrition resistant bodies, without the need to add a binder material.

The crystalline clay is formed from an aluminium source, a magnesium source,  
5 and, a silicon source. Usually saponite or montmorillonite is formed.

The shaped bodies can be prepared in various ways. In a preferred embodiment of the invention, an aluminium source, a magnesium source, and, a silicon source are combined in a slurry to form a precursor mixture.  
10 Subsequently, said precursor mixture is shaped. The resulting shaped bodies are aged, optionally after thermal treatment, in a liquid to obtain crystalline Mg-Al-Si-containing clay-containing bodies.

It is also possible to prepare a precursor mixture from only one or two sources source such as an aluminium source and/or a magnesium source, and/or a  
15 silicon source, shape it, and then add one or more additional other sources to the shaped bodies in any of the subsequent process steps. During the aging step, the various sources react to give the crystalline Mg-Al-Si-containing clay-containing bodies. Of course, it is also possible to use combinations of the two preparation routes described above, for instance: add the aluminium source  
20 and the magnesium source to form the precursor mixture, shape to form bodies, and then age the shaped bodies in a liquid containing a silicon source to form saponite- or montmorillonite-containing bodies.

Suitable alumina sources include aluminium oxides and hydroxides such as  
25 transition alumina, aluminium trihydrate (gibbsite, bayerite) and its thermally treated forms, including flash calcined alumina, sols, amorphous alumina, (pseudo)boehmite, aluminium-containing clays such as kaolin, sepiolite, hydrotalcite, and bentonite, modified clays such as metakaolin, alumina salts such as aluminium nitrate, aluminium chloride, aluminium sulfate, aluminium  
30 chlorohydrate, sodium aluminate. With the process according to the invention it

is also possible to use cruder grades of aluminium trihydrate such as BOC (Bauxite Ore Concentrate) or bauxite. When clays are used as an Al-source, it may be necessary to activate the alumina in the clay by acid or base treatment, (hydro)thermal treatment, or combinations thereof, etcetera. Acid treatment

5 comprises treatment with nitric acid, acetic acid, formic acid, phosphoric acid, sulphuric acid, hydrochloric acid, etcetera. Thermal treatment is usually performed at temperatures ranging from 30-1000°C, preferably 200-800°C, for a time ranging from several minutes to 24 hours, preferably 1-10 hours. Also mixtures of the above-mentioned aluminium sources can be used, and said

10 different aluminium sources can be combined in the precursor mixture in any sequence. It is also possible to add an aluminium source after the shaping step. In that case, the precursor mixture may already contain an aluminium source or not. If an aluminium source is added after the shaping step, it preferably is in liquid when contacted with the shaped bodies. This can be done

15 by dispersing or dissolving the aluminium source and adding it to the shaped bodies. Alternatively, the aluminium source can be added to the liquid in which the shaped bodies are aged. Also other aluminium sources than clay such as aluminium trihydrate may be pre-treated prior to the addition to the precursor mixture or prior to contacting it with the shaped bodies. Said pre-treatment may

20 involve treatment with acid, base treatment, thermal and/or hydrothermal treatment, all optionally in the presence of seeds or combinations thereof. It is not necessary to convert all of the aluminium source into crystalline clay. Any excess aluminium will be converted into silica-alumina, alumina (usually in the form of  $\gamma$  alumina or (crystalline) boehmite) and/or alumina-magnesia during

25 the aging step. These compounds improve the binding properties of the shaped bodies and may also provide different types of desirable functionalities for the bodies. For instance, silica-alumina and alumina provide acid sites for catalytic cracking and alumina (crystalline) boehmite also improves the nickel encapsulation capacity of the shaped bodies. The formation of, for example,

(crystalline) boehmite may be promoted by adding seeds, either in the precursor mixture or during aging.

Suitable magnesium sources include magnesium oxides or hydroxides such as MgO, Mg(OH)<sub>2</sub>, hydromagnesite, magnesium salts such as magnesium acetate, magnesium formate, magnesium hydroxy acetate, magnesium carbonate, magnesium hydroxy carbonate, magnesium bicarbonate, magnesium nitrate, magnesium chloride, magnesium-containing clays such as dolomite, sepiolite. Also mixtures of the above-mentioned magnesium sources can be used, and said different magnesium sources can be combined in the precursor mixture in any sequence and/or in any process step after the shaping step. If a magnesium source is added after the shaping step, it must be in liquid when contacted with the shaped bodies. This can be done by dispersing or dissolving the magnesium source and adding it to the shaped bodies. Alternatively, the magnesium source can be added to the liquid in which the shaped bodies are aged. The magnesium source may be pre-treated prior to the addition to the precursor mixture and/or prior to the addition to the shaped bodies. Said pre-treatment may comprise a thermal and/or a hydrothermal treatment, an acid treatment, a base treatment, all optionally in the presence of a seed, and/or combinations thereof. It is not necessary to convert all of the magnesium source into crystalline clay. Any excess magnesium will usually be converted to brucite or alumina-magnesia. For the sake of clarity, this excess of magnesium compounds in the shaped particle will be referred to in the description as magnesia. The presence of magnesia or alumina-magnesia in the shaped body may provide desirable functionalities to the shaped bodies. The presence of magnesia provides basic sites which render the shaped body suitable for removing or neutralising strong acid streams of gases or liquids.

Suitable silicon sources include sodium silicate and silica sol or mixtures thereof. Preferably a silica sol is used which does not introduce sodium in the

Mg-Al-Si-containing crystalline clay such as ammonium stabilised silica sol. If a silicon source is added after the shaping step, the silicon source must be in liquid when contacted with the shaped bodies. This can be done by dispersing or dissolving the silicon source and adding it to the shaped bodies.

- 5 Alternatively, the silicon source can be added to the liquid in which the shaped bodies are aged.

The various process steps will be described in more detail below.

#### 10 Preparation of the precursor mixture

In this step a precursor mixture is prepared from an aluminium source and/or a magnesium source and/or a silicon source in a liquid. In fact, all liquids are suitable, as long as they do not detrimentally interfere with the various sources.

- 15 Suitable liquids are water, ethanol, propanol, etcetera. The amount of liquid can be chosen such that a mixture with a milky substance is obtained, but also mixtures with a higher viscosity, for instance doughs, are suitable. If more than one source is used for the precursor mixture, the sources can be added as solids, but they can also be added in liquid. The various sources can be added
- 20 in any sequence. The preparation of the precursor mixture can be carried out with or without stirring, at room temperature or elevated temperature. Optionally, the precursor mixture is homogenised by, for instance, milling. Some conversion to crystalline clay may already take place upon combining the various sources, in fact, it is preferred that at least 5 wt% of the final total
- 25 amount of crystalline Mg-Al-Si- containing clay is already formed prior to shaping, but for the present invention it is essential that conversion also takes place after the shaping step. Usually more than 25wt%, preferably more than 50 wt%, more preferably more than 75 wt% and most preferably 80-95 wt% of the final amount of crystalline Mg-Al-Si-containing clay in the shaped body is
- 30 formed after the shaping step, because then shaped bodies with the highest

physical strength are obtained. The ratio Mg:Al may vary from 0.1 to 15, and the Mg:Si ratio may vary from 0.05 to 1.5. If desired, organic or inorganic acids and bases, for example for control of the pH, may be added to the precursor mixture or added to any one of the aluminium source, magnesium source and/or silicon source before these are added to the precursor mixture. An example of a preferred modifier is an ammonium base, because upon drying no deleterious cations remain in the anionic clay. Optionally, the precursor mixture is pre-aged prior to the shaping step. The pre-aging temperature may vary from 25 °C to 500 °C for a time ranging from 1 minutes to several days and may be conducted under atmospheric or increased pressure such as autogeneous pressure at temperatures above 100 °C.

### Shaping

Suitable shaping methods include spray-drying, pelletising, extrusion (optionally combined with kneading), beading, or any other conventional shaping method used in the catalyst and absorbent fields or combinations thereof. The amount of liquid present in the precursor mixture used for shaping should be adapted to the specific shaping step to be conducted. It might be advisable to (partially) remove the liquid used in the precursor mixture and/or add additional or other liquid, and/or change the pH of the precursor mixture to make the precursor mixture gellable and thus suitable for shaping. Various additives commonly used in the various shaping methods such as extrusion additives may be added to the precursor mixture used for shaping.

25



### Thermal treatment

After shaping the shaped bodies may optionally be submitted to a thermal treatment. Such a treatment increases the physical strength of the particles.

- 5 The thermal treatment can be conducted in an oxygen-containing atmosphere, in an inert atmosphere or in steam at temperatures varying from 30 to 1000°C for a time ranging from a few minutes to 24 hours. As in, for instance, spray-drying a thermal treatment is inherently involved, a further thermal treatment may not be necessary.

10

### Aging

In this step, the shaped bodies are immersed in a protic liquid or a protic gaseous medium. During the aging step crystallisation to crystalline clay takes place. Suitable protic aging liquids or gaseous media are those liquids and gaseous media in which the shaped bodies do not dissolve, such as water, ethanol, methanol, propanol, steam, gaseous water, gaseous ethanol, etcetera. Increasing the temperature of the liquid and/or the pressure can reduce the aging time. The aging can also be conducted under autogeneous conditions.

15

- 20 The aging temperature may range from 30 to 1000°C. The aging time can vary from 1 minute to several days, for instance 7 days. For some purposes it is advantageous to conduct several aging steps, optionally with intermediate drying steps, optionally followed by calcination steps. For instance, an aging step with a temperature below 100 °C may be followed by a hydrothermal aging step at a temperature above 100 °C and autogeneous pressure, or vice versa. As will be described below in further detail, additives can be added before, after or during any aging step.

25

- For some applications it is desirable to have additives present in and/or on the shaped bodies according to the invention, both metals and non-metals, such as

30

rare earth metals (e.g. Ce and La), Si, P, B, Group VI metals, Group VIII metals, noble metals such as Pt and Pd, alkaline earth metals (for instance Ca and Ba) and/or transition metals (for example Mn, Fe, Ti, V, Zr, Cu, Ni, Zn, Mo, Sn). Said metals and non-metals can be added separately or in mixtures in any  
5 of the preparation steps of the invention. For instance, they can easily be deposited on the shaped bodies before, during, or after aging, or else they can be added to the precursor mixture. Suitable sources of metals or non-metals are oxides, halides or any other salt, such as chlorides, nitrates, phosphates, etcetera. As mentioned above, the metals and non-metals may be added in any  
10 of the preparation steps. This can be especially advantageous for controlling the distribution of the metals and non-metals in the shaped bodies. It is even possible to calcine the shaped bodies, re-hydrate them and add additional additives.

With the help of additives the crystalline Mg-Al -Si clay-containing shaped  
15 bodies may be provided with desired functionalities, or the desired functionality may be increased by the addition of additives. The suitability of Mg-Al-Si clay-containing shaped bodies for the metal trapping in FCC may be improved by the addition of Zn. The presence of V and Zn improves the suitability for removal of S-compounds in the gasoline and diesel fraction of FCC.

20 The process according to the invention may be conducted batch-wise or in a continuous mode, optionally in a continuous multi-step operation. The process may also be conducted partly continuous and partly batch-wise.

25 The crystalline Mg-Al-Si clay-containing bodies may also be prepared to contain conventional catalyst components such as matrix or filler material (e.g. clay such as kaolin, titanium oxide, zirconia, alumina, silica, silica-alumina, bentonite etcetera), molecular sieve material ( e.g. zeolite Y , ZSM-5 etcetera). Said conventional catalyst components may be added prior to the shaping step.

30 Because the Mg-Al-Si clay is formed in situ, the resulting body will have a

homogeneous dispersion of anionic clay and catalyst components. With the method according to the invention, multiply functional bodies can be prepared which can be used as a catalyst or as a catalyst additive.

- 5 If desired, the crystalline Mg-Al-Si-containing clay-containing shaped bodies prepared by the process according to the invention may be subjected to ion exchange to change the chemical and physical properties of the clay. Said ion exchange can be conducted as soon as the crystalline clay has been formed. Suitable ion exchange compounds include any metal cation containing  
10 compound such as compounds containing Cu, Al, Mg, Zn, pillaring cations such as aluminum chlorohydrol, transition metals, e.g. Ni, Rare earths etcetera.

- The present invention is further directed to crystalline Mg-Al-Si-containing clay-containing shaped bodies obtainable by the process according to the invention.
- 15 As mentioned above, the shaped bodies appear to have high mechanical strength and attrition resistance, comparable with that of Mg-Al-Si-containing clay-containing bodies prepared by dispersing clay into a matrix or binder material and then shaping the clay-containing composition, yet without matrix or binder material having to be added to the crystalline clay. This means that  
20 with the process according to the invention, crystalline Mg-Al-Si-containing clay-containing shaped bodies can be prepared containing more than 50 wt%, preferably more than 70 wt %, or even more preferably more than 90 wt% crystalline clay. Although binder material may be present in the shaped crystalline clay containing bodies according to the invention, for instance as a  
25 result of an excess aluminium source present in the precursor mixture, any binder that is present in the shaped bodies according to the invention will be present as a discontinuous phase, as is depicted schematically in Figure 1. This is in contrast to Mg-Al-Si-containing clay-containing bodies prepared in the conventional way, i.e. by embedding clay into a matrix or binder material,  
30 where the binder material in the bodies is present in a continuous phase, as is

schematically depicted in Figure 2. It is of course also possible to incorporate the crystalline Mg-Al-Si-containing clay-containing shaped bodies into a matrix. In that case, composite particles are obtained which comprise crystalline Mg-Al-Si-containing clay-containing shaped bodies with, optionally, binder material  
5 in a discontinuous phase, embedded in a binder material, as is schematically depicted in figure 3.

Figure 1: Schematic view of a shaped body according to the invention

Figure 2: Schematic view of a shaped body according to the prior art

10 Figure 3: Schematic view of a composite particle comprising shaped bodies according to the invention

In Figure 1 a schematic view is given of a shaped crystalline Mg-Al-Si-containing clay-containing body (1) according to the present invention which  
15 comprises crystalline clay (2) and binder material (3) in a discontinuous phase.

In Figure 2 a schematic view is given of a shaped crystalline Mg-Al-Si-containing clay-containing body (1) according to the prior art which comprises crystalline clay (2) and binder material (3) in a continuous phase.

In Figure 3 a schematic view is given of a composite particle comprising  
20 crystalline Mg-Al-Si-containing clay-containing shaped bodies (1) which comprise crystalline clay (2) and binder material (3) in a discontinuous phase which are embedded in binder material (3') which is in a continuous phase.

## Claims

1. Process for the preparation of crystalline Mg-Al-Si-containing clay-containing bodies from sources comprising an aluminium source, a magnesium source, and, a silicon source, comprising the steps of:
  - a) preparing a precursor mixture,
  - b) shaping the precursor mixture to obtain shaped bodies,
  - c) optionally thermally treating the shaped bodies, and
  - d) aging to obtain crystalline Mg-Al-Si-containing clay-containing bodies.
2. Process according to claim 1 wherein in step a) an aluminium source, a magnesium source, and a silicon source are combined to obtain a precursor mixture.
3. Process according to claim 1 or 2 wherein an aluminium source is present in the precursor mixture and a magnesium source is added after the shaping step b).
4. Process according to claim 1 or 2 wherein a magnesium source is present in the precursor mixture and an aluminium source is added after the shaping step b).
5. Process according to any one of the preceding claims wherein an aluminium source is present in the precursor mixture and a silicon source is added after the shaping step b).
6. Process according to any one of the preceding claims 1-5 wherein the magnesium source and/or the alumina source is pretreated prior to being added to said precursor mixture or prior to being added to said shaped

bodies, said pre-treatment comprising a thermal treatment, a hydrothermal treatment, an acid treatment, a base treatment or a combination of one or more of said treatments.

- 5     7.     Process according to any one of preceding claims 1-6 wherein the aluminium source comprises aluminium trihydrate or its thermally treated form.
- 10     8.     Process according to any one of preceding claims 1-7 wherein the aluminium source comprises (pseudo)boehmite.
9.     Process according to any one of claims 1-7 wherein the aluminium source comprises an aluminium salt.
- 15     10.    Process according to any one of claims 1-7 wherein the aluminium source comprises an amorphous alumina gel.
11.    Process according to any one of claims 1-7 wherein the aluminium source comprises kaolin.
- 20     12.    Process according to any one of the preceding claims wherein the magnesium source comprises magnesium oxide.
13.    Process according to any one of the preceding claims wherein additives are added in step a).
- 25     14.    Process according to any one of the preceding claims wherein additives are added after the shaping step b).

15. Crystalline Mg-Al-Si-containing clay-containing shaped body obtainable by any one of the processes of claims 1-13.
- 5 16. Process according to any one of claims 1-14 wherein the precursor mixture is pre-aged prior to the shaping step at a temperature from 25<sup>0</sup> C to 500<sup>0</sup> C for a time from 1 minute to several days and under a pressure from atmospheric to an autogeneous pressure at temperatures above 100<sup>0</sup> C.
- 10 17. Process according to any one of claims 1-14 and 16-18 wherein step c) is conducted in several aging steps with drying and calcining following each aging.
- 15 18. Process according to any one of claims 1-14 and 16-18 wherein the shaped bodies may be provided with desired functionalities by addition of appropriate additives.
- 20 19. The process of claim 1 conducted batch-wise, continuous or partly continuous and partly batch-wise.
- 20 20. The process of claim 1 conducted in a continuous multi-step operation.
21. The process of claim 1 wherein additional components such as matrix or filler material are added prior to shaping step b).
- 25 22. Crystalline Mg-Al-Si-containing clay-containing body wherein any binding material present in the body is present in a discontinuous phase.

23. Composite particle comprising a crystalline Mg-Al-Si-containing clay-containing body according to claim 15 which is embedded in binder material.



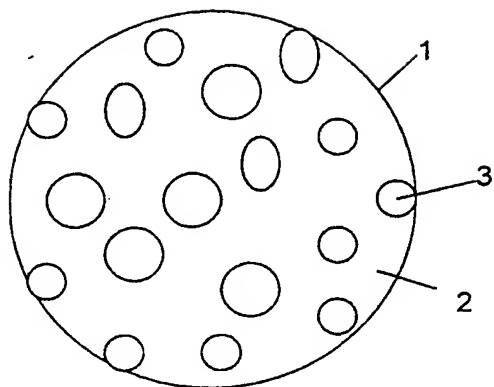


Fig. 1. Shaped body according to the invention

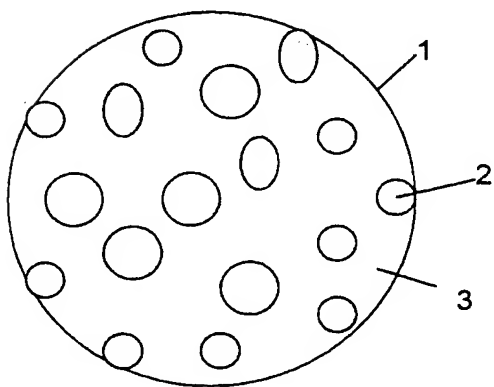


Fig. 2. Shaped body according to the prior art

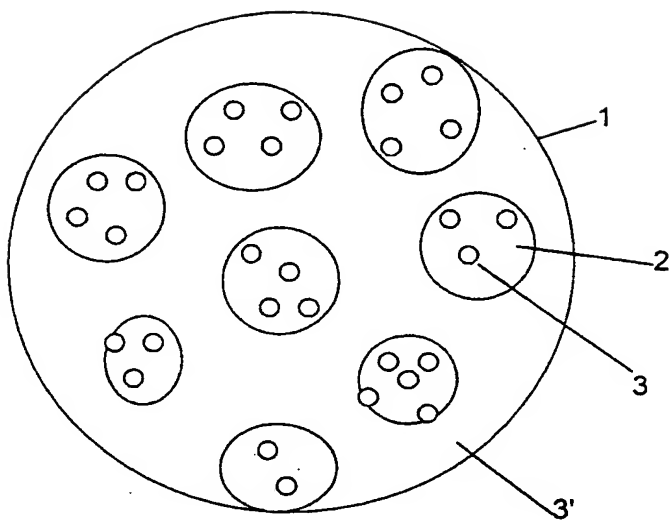


Fig. 3. Composite particle comprising shaped bodies according to the invention

# INTERNATIONAL SEARCH REPORT

Intern. Application No  
PCT/EP 00/07785

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 B01J21/16 B01J37/00 C04B33/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 B01J C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)  
EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 300 469 A (DEEBA MICHEL ET AL) 5 April 1994 (1994-04-05)	
A	FR 2 289 095 A (GOBERT MAX) 21 May 1976 (1976-05-21)	
A	WO 96 04990 A (THIELE KAOLIN CO) 22 February 1996 (1996-02-22)	
A	DE 44 05 876 A (SUED CHEMIE AG) 5 October 1995 (1995-10-05)	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

28 November 2000

Date of mailing of the international search report

11/12/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040. Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Thion, M

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/07785

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5300469 A	05-04-1994	AT 177466 T AU 664009 B AU 5685794 A CA 2144544 A CN 1093951 A, B DE 69323896 D DE 69323896 T EP 0673404 A ES 2128546 T JP 8504397 T WO 9413755 A US 5384041 A	15-03-1999 26-10-1995 04-07-1994 23-06-1994 26-10-1994 15-04-1999 16-09-1999 27-09-1995 16-05-1999 14-05-1996 23-06-1994 24-01-1995
FR 2289095 A	21-05-1976	NONE	
WO 9604990 A	22-02-1996	US 5711930 A AU 3279195 A US 5866496 A US 5925327 A	27-01-1998 07-03-1996 02-02-1999 20-07-1999
DE 4405876 A	05-10-1995	NONE	